

Overview

on

Particulate Matter



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SUMMARY

Lately attention and interest have been given to the particulate matter (PM) issues. Studies have shown that the concentration of particles in ambient air is correlated with adverse human health effects. In Canada, both Federal and Provincial governments are working on the development of national ambient PM₁₀ and PM_{2.5} objectives. These objectives have the purpose of protecting human health as well as the environment.

Many projects associated with the characterization of the particulate emissions are currently ongoing in Alberta. These projects were initiated by industries that have recognized the importance of controlling PM emissions and the potential impact of PM regulations on their industrial operations.

Source apportionment, which provides estimates on the particulate matter contribution of various sources to the ambient levels, is an important component necessary for achieving desired ambient air quality objectives.

The most common source apportionment method for particulate matter is called Chemical Mass Balance (CMB) based on ambient information and source emission profiles. Ambient PM samples are being collected by Alberta Environmental Protection in Edmonton and Calgary with Environment Canada analyzing the samples. However, there is no Alberta-specific source emission profile database currently available.

Alberta Environmental Protection (AEP) initiated the Alberta Source Apportionment and Source Emission Profile Study to coordinate research efforts related to emissions from various sources and develop a comprehensive source emission profile database.

The purpose of the literature search is to review and comment on the available information on PM source emission profiles and source apportionment methodology, and identify, in consultation with stakeholders and AEP, data gaps that may require further field studies.

This report has two parts. The first presents a detailed description of the sampling and analytical methodologies. The second concentrates more on a brief description of the common apportionment studies with emphasis on the chemical mass balance (CMB), and a compilation of source apportionment studies performed in Canada and around the world.

Sampling particulates from various sources is a very critical procedure. It should be performed with extreme care. For this reason, particulate sampling methods, for point and area sources, were presented and described. Sampling systems were also listed with description of their operations. The systems were the cascade cyclone sampler, the cascade impactor, the BOVAR FL-RT1 sampler and the EPA Method 5 train.

Chemical profiles are crucial for any apportionment study. A detailed description of all the analytical methods that are used for analysis of heavy metals, soluble ions and organic and elemental carbon was outlined. Organic compound analysis was also described. The organics could include polycyclic aromatic hydrocarbons (PAHs), alkanes, aldehydes, ketones, and acids. The PM physical parameters of size distribution, shape and solubility was also presented. Recommendations on the analytical methods to be used for particulate analysis were proposed.

For any apportionment study, both source and receptor models have to be used to quantify the source contributors to ambient PM concentrations. But for preliminary studies only receptor models using the chemical composition of source emissions and receptor concentrations could be considered. The chemical mass balance (CMB) receptor model uses source profiles (i.e., the fractional amount of each chemical in source emissions) and ambient concentrations of

chemicals measured at PM sampling sites as model inputs. A mass balance is constructed in which the concentration of specific chemical constituents in a given ambient sample is described as arising from a linear combination of the relative chemical compositions of the contributing sources.

For the CMB receptor model to be successful, the following conditions and criteria have to be met. (1) The chemical compositions of both the source sample and the ambient samples are known from experimental measurements; and the chemical species measured at sources and receptors are comparable. (2) The chemical species for which mass balance equations are written must be sufficiently stable that they are conserved during transport from their sources to the receptor air monitoring sites. The species must neither be significantly depleted from the particulate fraction by volatilization or chemical reaction, nor be significantly increased by atmospheric chemical transformation processes. (3) The number of chemical constituents included in the mass balance calculations must be equal to or larger than the number of sources. (4) All major sources of each chemical species used in the mass balance must be included in the model. The relative chemical compositions of the emissions from different source types must be different from each other in a statistical sense such that the problems of source profile co-linearity are avoided. (5) The amount released into the atmosphere from a source must be large enough, so that the atmospheric concentration of the chemical species under consideration is quantifiable by the analytical method used.

A description of the CMB model, its assumption, limitations, and results of source apportionment studies performed around the world were presented.

Finally, data gaps were identified. Effort towards generating Alberta specific source profiles should be made for the next phase of this project.

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INTRODUCTION

Background

Pollution from airborne particulate matter (PM) is rapidly becoming one of the most important environmental issues of the 1990s. There is a growing body of evidence suggesting that ambient airborne PM levels are strongly associated with adverse health effects, ranging from asthma to human mortality (U.S. EPA, 1996). These human health effects are found to correlate with the ambient particulate levels of less than 10 μm aerodynamic diameter (PM_{10}) and more specifically, its fine fraction, with particles less than 2.5 μm aerodynamic diameter ($\text{PM}_{2.5}$).

Federal and provincial governments in Canada are currently working on national PM_{10} and $\text{PM}_{2.5}$ objectives for protecting human health and the environment. These national objectives will take into consideration all scientific, social-economic and technical aspects while being developed; provincial processes will be initiated to develop provincial guidelines.

Many Alberta industries have recognized the importance of controlling the PM emissions, the potential impact of PM regulations on their industrial operations, and the need in developing strategies to meet the Alberta ambient PM guidelines. AEP initiated, in cooperation with various different levels of government, project to coordinate PM source emission characterization.

Source apportionment, also called receptor modeling, provides estimates on the contributions of different sources to the receptor. It is an important tool for developing and achieving ambient air quality objectives. The results of the source apportionment can be used to evaluate emission reduction on the ambient PM levels, to devise more efficient emission reduction strategies and to provide the necessary information for the development of Alberta ambient PM guidelines. There are techniques for several source apportionment or receptor modeling. The most widely used for the apportionment of particulate matter is

the Chemical Mass Balance (CMB) (Watson, 1979, 1984, 1990, 1997). This method uses ambient information and source emission profiles.

In gathering information on airborne PM measured in Alberta, data deficiency was identified. A source apportionment study was completed by Environment Canada in 1984 for selected Canadian cities (Environment Canada, 1994). Since then, major changes in source emission profiles have occurred due to vehicle fuel modifications, the presence of new types of industry and new pollution control measures. Limited studies have been carried out in British Columbia (Lowenthal et al., 1997) and southern Ontario (Ontario Ministry of Environment and Energy, 1995). But the results of these studies may not be directly adopted in Alberta, because of different major sources or different source profiles.

Objectives

The purpose of this study is to:

- (1) Review the sampling and analytical methodologies for particulate matter.
- (2) Review the available source apportionment methodologies.
- (3) Provide a compilation of source apportionment studies in Canada and elsewhere.
- (4) Identify data gaps and recommendation for future work.

PART I

SAMPLING AND ANALYSIS METHODOLOGIES

1. SOURCE SAMPLING METHODS FOR CHEMICAL ANALYSIS

Receptor models for particulate source apportionment require accurate, precise and compatible data sets of ambient PM chemical concentrations at the receptor and major source PM chemical composition profiles. Sampling for chemical analysis requires stringent attention to the PM size fraction to be collected, chemical constituents to be measured, analytical methods to be used, filter media, sample handling, sample storage, and to the sampler used to obtain the PM deposits or the PM filter deposits. Thus, the standard sampling methods applied to PM source emissions for compliance purpose do not necessarily meet the needs of other or additional purposes such as chemical speciations for PM₁₀ and PM_{2.5}. These methods need to be enhanced when chemical analyses are required (U.S. EPA, 1996).

For the purposes of sampling, particulate sources may be categorized into the following four groups (Houck, 1991):

- (1) High-temperature point sources such as industrial-type stacks, vehicular exhausts and woodstoves.
- (2) Low-temperature point sources, such as ventilation exhausts and ducts.
- (3) Process fugitive sources, including a wide range of industrial, agricultural, forestry, and area sources, such as field burning, unducted industrial roof-top emission, construction and demolition activities, stockyards, ore crushing and forest fires.
- (4) Passive fugitive sources, including wind-blown dust from roadways, parking lots, agriculture fields, dry lake beds and industry storage piles, and dust suspended by vehicular traffic (due to sampling methods used similar to those used for wind-blown dust).

Sampling methods used for each group are briefly discussed below.

1.1 High-Temperature Point Sources

Sampling methods used for high-temperature point sources including the diluting sampling, plume sampling, conventional direct sampling, cascade cyclone sampler, cascade impactor sampler and EPA Method 5.

1.1.1 Dilution Sampling

Dilution samplers have been under development for over two decades (Heinsohn et al. 1980). Its principal objective is to obtain chemical data representative of particulate emissions after mixing and cooling with the atmosphere has occurred.

A schematic diagram of the source dilution sampler is shown in Fig. 1. A commercial large source dilution sampler, URG Model 3000R, from URG (Chapel Hill, NC 27516) is illustrated in Fig. 2 (URG, 1996). Basically, a dilution sampler consists of an in-stack probe, a dilution chamber and dilution air control unit, size-categorized samplers, sampling pump and control units. The hot stack gases are drawn isokinetically through the in-stack probe into the dilution chamber where they are mixed with filtered ambient air. After an aging period, typically 20-30 seconds at a dilution ratio of 10 to 40 to allow for the process of condensation onto particle surfaces, particles are drawn through a size selective inlet and collected onto the filter substrates for subsequent chemical analysis. Particulate material on multiple substrates for different chemical analyses can be obtained simultaneously or through sequential sampling of the same gas stream.

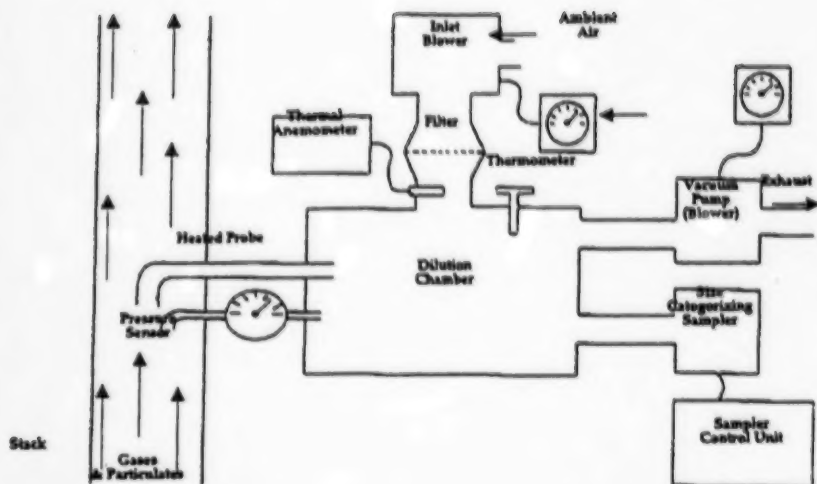


Figure 1. Schematics of a dilution sampling system.

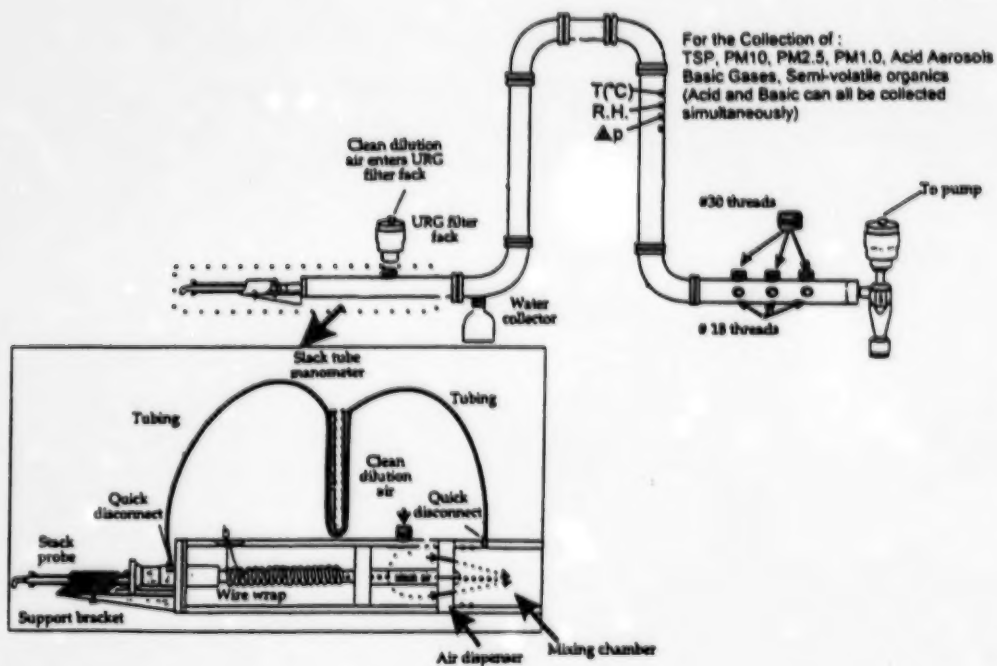


Figure 2. A commercial large source dilution system. URG 3000 model 3000 R (URG, 1996).

The dilution sampling method has two obvious advantages for reception modeling. First, it partially simulates processes occurring in upper portions of the stack and in the plume leaving the stack, where condensation, coagulation, and chemical reactions occur as stack gases are cooled. Secondly, using this method, the same sampling substrates, devices and analytical techniques used in ambient sampling can be used. As a result, biases resulting from the use of separate sampling systems in source apportionment studies are eliminated.

Dilution sampling systems have been used for several air quality studies (Hildemann et al., 1991; Rogge et al., 1991, 1993a and 1993b; Schauer et al., 1996; Olmez et al., 1988). In one early study, elemental composition in refinery PM emissions collected by the dilution sampling method and the conventional "hot" temperature sampling method were compared (Olmez et al., 1988). Except for sulfur, no significant differences were observed for other elements studied, perhaps due to the large uncertainties of the experimental data (Olmez et al., 1988). Recently, in a preliminary study for particulate matter from residual fuel oil fired boiler (Lee et al., 1997), the mass loading of total suspended particulate obtained using the dilution sampler is nearly doubled compared to that obtained using one conventional "hot" temperature direct sampling method (see section 1.1.3.1). This was mainly attributed to the incomplete condensation of sulfur-containing species and evaporative loss of volatile organic components on the hot filter of the direct sampling.

The inherent disadvantage of the dilution sampling method is that it is a forced dilution process, by which the particulate collected may be different from that collected from the stack plume. Also, the operation of a dilution sampling system is more complex. At present, a few commercial dilution samplers, such as Model 3000R from URG (Chapel Hill, NC 27516), are available. The operation of the dilution system may not be so easy to operate. But recently Dr. Lee's

group at CAMET in Ottawa (Lee et al. 1997), in collaboration with TransAlta Corporation (I. Liepa, Personal Communication, 1997), has been successfully applied the dilution sampling method for PM emissions projects.

1.1.2 Plume Sampling

The plume sampling method permits sampling after dilution and cooling. This is usually achieved by airborne sampling from airplane (Richards et al., 1985), tethered balloons (Shah et al., 1988), helicopters or platforms. Figure 3 illustrates a plume sampling from a platform, in which hydrocarbons emissions were collected on a glass fiber filter and a polyurethane foam cartridge (Strosher, 1996).



Figure 3. An illustration of plume sampling (Strosher, 1996).

Plume sampling is generally more expensive and is perhaps more appropriate for small industrial stacks and sources such as residential wood

combustion (Houck et al., 1987). The inherent problem associated with this approach is the presence of background pollutants in the ambient air. It must be confirmed that the impact of background air for all chemical species of interest is negligible compared to the concentrations originating from the point source.

1.1.3 Conventional "Hot" Temperature Direct Sampling

Many emission profiles listed in the SPECIATE database (U.S. EPA, 1993) were collected by the conventional direct sampling methods, such as sampling using the in-stack cascade cyclone samplers, the in-stack cascade impactor samplers, and EPA Method 5 (Wight, 1994).

These sampling methods collect PM directly from the hot stack gases. Thus, the samples collected may not yield an accurate representation of the chemical composition and size distribution of particle leaving the stack, especially for volatile inorganic species such as Hg, S, As and Se and the volatile and semi-volatile organic species.

1.1.3.1 The Cascade Cyclone Sampler

The in-stack cascade cyclone sampling system (Richards, 1996) generally consists of a probe, a series of cyclones, a backup filter, a pump and a control unit. Each cyclone has a specified particulate cut point. Particles suspended in the stack gas are sampled isokinetically through the probe and into the first cyclone body tangentially creating a vortex. Centrifugal forces cause particles larger than the PM size cut point of the cyclone to move outward to the walls of the cyclone and into a collection cup. The next cyclone has smaller dimensions, thus the gas velocity increases and smaller particles are collected, and so on for each successive cyclone. The particles uncollected by the last cyclone are caught at the backup filter.

U.S. EPA method 201A uses a cyclone sampling system for PM₁₀ emission test measurements. Recently, a draft test protocol for measurement of particulate emissions in both PM₁₀ and PM_{2.5} size categories and for subsequent chemical

analysis has been developed under the contract with the Portland Cement Association (Richards, 1996). This protocol is a modified version of U.S. EPA Method 201A. The protocol uses a sampling system equipped with two cyclones. The first cyclone with a PM size cut point of 10 μm diameter collects the $>10 \mu\text{m}$ fraction. The second one with a 2.5 μm cut point collects the 2.5 – 10 μm fraction. The fraction smaller than 2.5 μm is collected on the backup filter. The cyclone cup can hold particulates from 1-2 g. The backup filter can hold particles from 2-5 mg. This protocol not only tests the PM_{10} and $\text{PM}_{2.5}$ emission factors, but also addresses the chemical composition testing.

1.1.3.2 The Cascade Impactor Sampler

The in-stack cascade impactor sampling system generally consists of a probe, a series of plates, a backup filter, pump and the control unit. Each of the plates has holes or slots of known diameter or dimension. Each successive plate or stage has either fewer or smaller openings. Stack emission is withdrawn isokinetically from the source through the probe and then through the succeeding orifice stages with successively high orifice velocities. Successively smaller particles are inertially impacted onto the collection plates and the particles uncollected by the last collection plate are caught in the backup filter.

This sampling device allows the collection of different particulate size fractions to determine the particulate size distribution. The primary limitations of impactor samplers are particle bounce, overloading of collection stages and interstage losses (Marple et al., 1993). Using this method, the maximum allowable amount of particulate in each size fraction is about 2 mg; and the PM size fractions collected for the mean particulate aerodynamic diameter vary with the flow rate through the inlet.

1.1.3.3 The BOVAR FL-RT1 Sampling System

The BOVAR FL-RT1 sampling train system (Bovar Environmental, 1995) has been used in Alberta for research projects. This system is specially designed

by BOVAR Environmental to collect isokinetically a large amount of representative total suspended particles (TSP) (5-50 g) from the stack, in order to support several research projects for the power and utility industry in Alberta (F. Goodarzi, Personal Communication, 1997). As the train can be equipped with an external high flow cascade impactor, particle distribution measurement over 5 size fractions can also be performed.

It should be noted that any sampler involving cyclone (paragraph 1.1.3.1) and impaction technique (paragraph 1.1.3.2) require a constant flow rate to collect the designed PM size fractions. The isokinetic sampling for stack emissions can be achieved initially, but is difficult to maintain during the whole sampling period.

1.1.3.4 EPA Method 5

EPA Method 5 provides the procedure of sampling stack emission from stationary sources using a standard sampling train which is commonly used to measure emissions of various particulate and gaseous metals. Alberta Environmental Protection (Alberta Stack Sampling Code, 1995) and Environment Canada (Environment Canada, 1993a) have adopted this method for emission compliance testing.

In EPA Method 5, stack emission is withdrawn isokinetically from the source and total suspended particles (TSP) is collected on a filter maintained at a temperature of $120 \pm 14^{\circ}\text{C}$. The volatile and gaseous species passed through the filter are collected in a series of chilled impingers containing dilute nitric acid and hydrogen peroxide, or acidic potassium permanganate solutions. Sampling train components are recovered and analyzed for toxic metals.

EPA method 5 can not be used for the collection of different particulate size fractions without modification.

1.2 Low-Temperature Point Sources Sampling Methods

Point sources at near ambient temperature are defined as low-temperature sources for the purpose of sampling. Sampling the low-temperature point sources is relatively simple, as compared to high-temperature point sources. Since emissions occur at near ambient temperature at which condensation may not be an issue, dilution sampling is generally not required and size-categorized ambient sampling devices (Chow, 1995) can be adopted. These devices are usually positioned into the flow stream and the isokinetic sampling is approximated, and a flow collimating tube is used with an inlet diameter that is the same size as the exposed diameter of standard filters which are employed.

In some cases, a dilution sampling system is still used with low-temperature point sources due to a high condensed water droplet content which can be deleterious to samplers collected on filter substrates. The filtered ambient air introduced to the dilution system permits the water droplets to evaporate prior to sample collection.

1.3 Sampling Methods for Process Fugitive Emissions

Process fugitive emissions are defined, for the purpose of sampling strategy, as those emissions which were produced by active processes.

Typically, ground-based samplers are used for sampling the continuous or intermittent process fugitive emissions. In some cases, aircraft and balloon samplers have been used (Shah et al., 1988). Usually, ground-based and size-categorized fugitive source samples are collected in an analogous fashion to ambient samples. The position of the ground-based sampler inlet in the plume or path of source particles is often accomplished with custom-made brackets, extension tubes, or platforms. In some cases, simply situating the samplers on a roof or on a topographic high point is adequate. In each case, the samplers are situated in the aerosol plume, with care being taken to minimize contamination from other sources. Due to the heavier particulate concentrations near the

source, a shorter sampling duration is required to achieve optimal filter loading. A number of short-duration samples can be taken, analyzed and the analytical data averaged. For agricultural burning of crop residues, the particle inlet of the ground-based sampler has been located 2 to 5 meters above the ground level. For forestry burning, samplers have been located 10 to 15 meters above the fuel (Houck, 1991).

1.4 Sampling Methods for Passive Fugitive Emissions

Passive fugitive emissions are defined, for the purpose of sampling strategy, as those sources where wind or vehicular activities produce dust from exposed surfaces.

In addition to ground-based sampling as discussed in section 2.4, grab sampling and vacuum sampling followed by laboratory drying and sieving (to less than 38 μm particles) and re-suspension have been used for the passive fugitive emissions. Ambient particle size-categorized sampling devices are used in the specially designed re-suspension chamber to collect the particle size fractions (Chow et al., 1994). The vacuum sampling is often required as oppose to the grab sampling, because it collects effectively the relatively small amount of dust remaining on the pavement surface. To reduce the total number of individual samples, bulk samples are often composited, prior to resuspension and measurements.

The criteria for road selection for sampling includes proximity to receptor sites, traffic patterns, industrial activity, wintertime sanding or salting, and the chemical composition of the surrounding soils, road-fills and cuts, and shoulder gravel characteristics.

1.5 Filter Media

The filter characteristics usually considered are:

- (1) Sampling efficiency – should remove more than 99% of particles drawn through them, regardless of particle size or flow rate.
- (2) Mechanical stability – should be flat, remain one piece, provide good seal with the sampler to eliminate leaks.
- (3) Chemical stability – should not be chemically reactive with the deposit, will not absorb gases that not intended to be collected, but adsorb, at near 100% efficiency, gases when it is desired.
- (4) Temperature stability – should retain the porosity and structure at temperatures typical of the sampled source emission or airstream.
- (5) Flow resistance and loading capacity – should not have very high flow resistance, to allow sufficient amounts of air to be drawn through them to satisfy the flow rate requirements of the inlet and to obtain an adequate deposit.
- (6) Cost and availability – should be consistently manufactured and available at reasonable cost.
- (7) Blank concentrations – should have low blank mass level and should not contain significant and highly variable concentrations of the chemicals which are being determined by the analytical method.

In general, one filter media may not be suitable for the analysis of all chemical species. For example, Teflon membrane filters are suitable for the analysis of elements/metals and soluble ions, due to the low blank elemental concentrations. But Teflon filters contain carbon. Therefore, they are not suitable for the analysis of elemental carbon or organic carbon. Pre-baked quartz or glass filters are suitable for the analysis of elemental carbon or organic carbon. But quartz or glass filters may not be suitable for the analysis of many elements, due

to the relatively high blank levels, especially for the glass elements of Al, Si, B, Fe, Na etc. Detailed comparisons of various filter media are available from references (Chow, 1995; U.S. EPA, 1996; U.S. EPA, 1994).

1.6 Recommendations

- (1) The chemical compositions of source PM size fractions with aerodynamic diameters of less than 2.5 μm (PM_{2.5}) and 2.5-10 μm or 0-10 μm (PM₁₀) should be determined for receptor modeling. These two fractions are comparable with the natural fine and coarse modes of PM and with the ambient PM size fractions in which chemical composition data in Alberta are available (Alberta Environmental Protection, 1996). The measurement of chemical compositions of source PM size fractions with aerodynamic diameters greater than 10 μm (or total suspended particles) can be optional. Ambient PM chemical composition data for this fraction is currently not available in Alberta. However, there are many source profiles of this fraction found in the literature.
- (2) For high-temperature point source emissions, dilution sampling seems to be the preferred choice as it provides more accurate results in terms of chemical composition, particle size distribution and mass loading. It partially simulates processes occurring in upper portions of the stack and in the plume leaving the stack. However, the added benefit for CMB modeling is unclear. Some of the additional volatile species collected may undergo chemical reactions in the atmosphere. Some species collected in ambient samples may have high uncertainties due to their high volatile nature. Studies are being carried out in Canada and the US in further examining the method.
- (3) Besides the dilution system the Anderson cascade cyclone system

(section 1.1.3.1.) would be the system of choice. It can collect particles at the in-stack temperature for each size fraction of PM_{2.5} and 2.5-10 µm and greater than 10 µm. A protocol of this sampling method, which is a modified EPA method 201A (EPA Emission Measurement Branch Method EMTIC TM-201A), is available (Richards, 1996).

2. ANALYTICAL METHODOLOGIES FOR NON-ORGANIC PARAMETERS

The non-organic parameters to be determined can be divided into the following classes: (1) mass; (2) elements; (3) water-soluble ions, (4) physical properties: shape and solubility. The discussion on the analyses of total elemental carbon will be presented in section 3.2 together with the discussion on the analysis of organic carbon.

2.1 Mass Measurement

Mass measurement is the most common measurement on aerosol samples. The data is used to calculate the particulate mass concentration (µg/m³) and/or the composition profiles (µg/g).

The PM mass is often measured by gravimetry. The net PM mass on a filter is determined by weighing the filter before and after sampling with an electrobalance in a temperature and relative humidity controlled environment. The minimum readability of the balance should satisfy the net mass to be determined. One of the requirements from the recent U.S. EPA reference method for PM_{2.5} (U.S. EPA, 1997) is that prior to the gravimetric measurement, filters should be conditioned for 24 hours at a constant (within 5%) relative humidity between 30% and 40% and at a constant temperature (within ± 3 C) between 15 C and 30 C. These limits are intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species.

2.2 Elemental Analysis

Elemental analysis for airborne PM generally refer to the measurements for total concentrations of multi-elements (e.g. 20-60 elements), as opposed to extractable or dissolved concentrations of these elements.

Photon-induced X-ray fluorescence (XRF) spectrometry, proton induced X-ray emission spectrometry (PIXE), instrumental neutron activation analysis (INAA), inductively coupled plasma atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) have all been applied to elemental measurements of aerosol samples (U.S. EPA, 1994). In addition, inductively coupled plasma mass spectrometry (ICP-MS) has been applied in recent years (Wang et al., 1995; Jalkanen et al., 1996).

2.2.1 X-Ray Fluorescent (XRF) and Proton-Induced X-Ray Emission (PIXE) Spectrometry

In XRF (Torok et al., 1994) and PIXE (Nelson, 1977), the filter deposit is irradiated by high energy X-rays (for XRF) or protons (for PIXE) which eject inner shell electrons from the atoms of each element present in the sample. When a higher energy level electron drops into the vacant lower energy orbital, a fluorescent X-ray photon is released. The energy level of this photon is unique to each element, and the number of photons is proportional to the concentration of the element in the sample. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

Depending on the types of detectors used, XRF methods can be divided into two categories: wavelength dispersive XRF (WDXRF) uses crystal diffraction for detection and energy dispersive XRF (EDXRF) uses a silicon semiconductor detector. The WDXRF method has high spectral resolution, which minimized peak overlaps, but requires high power excitation to overcome low sensitivity resulting in excessive sample heating and potential degradation. Conversely, the

EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures. Depending on the X-ray sources, XRF methods can be further categorized as direct excitation and secondary target excitation. The latter produces a more nearly monochromatic excitation, which reduces unwanted scatter from the filter, yielding better detection limits.

XRF methods determine the total concentration of multi-elements simultaneously, and are generally considered as nondestructive method, allowing subsequent analyses of the sample by other methods. However, it generally requires an uniform deposition on the filter for quantitative measurement. Also, emitted X-rays with energies less than ~4 keV, such as that emitted from elements Na, Mg, Al, Si, P, S, Cl and K, can be absorbed in the filter and in a thick particle deposit, causing poor detection limits. Very thick filters also scatter much of the excitation radiation or protons, resulting in poor detection limits for XRF and PIXE.

The total concentrations for more than 50 elements in particulate matter collected from the ambient monitoring sites in Edmonton and Calgary have been determined using EDXRF by Environment Canada Laboratories which is a part of the National Air Pollutant Surveillance (NAPS) Program (Alberta Environmental Protection, 1996).

2.2.2 Instrumental Neutron Activation Analysis (INAA)

In INAA (Ondov and Divita, 1993), a sample is irradiated in the core of a nuclear reactor (such as a slowpoke) for periods ranging from a few minutes to several hours. The neutron bombardments transform many elements into radioactive isotopes. The energies of the gamma rays emitted by these isotopes are unique to the corresponding isotopes, and hence, identify them and their parent elements. The intensity of the gamma rays is proportional to the amount of the parent element present in the sample. Different irradiation times and

cooling periods (up to 20-30 days) are used before counting with a germanium detector.

Similarly to XRF, INAA is capable of determining total concentrations of multi-elements simultaneously. However, INAA does not quantify some of the abundant species in ambient PM such as Si, Ni, Sn and Pb. Also, INAA requires a nuclear reactor. While INAA is technically nondestructive, sample preparation involves folding the sample tightly and sealing it in plastic and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses.

2.2.3 Atomic Absorption Spectrometry (AAS)

In AAS (Ranweiler and Moyers, 1974), the sample is first extracted/digested in a strong hot acid mixture to digest/dissolve the solid material. A few milliliters of the extracted/digested solution are introduced to a flame (FAAS) or a graphite furnace (GFAAS), where the sample is vaporized and atomized. Most elements absorb light at specific wavelength in the visible spectrum. A light beam with wavelength specific to be absorbed by the element being measured is passed through the flame or the graphite furnace, and then detected by a monochromator at a selected wavelength. The extent of the light absorbed is related to the concentration of the element in the sample. By comparing with the absorption from known standards, the concentration of the element in the sample is quantified. The detection limits of GFAAS are about 10 to 100 fold of lower (i.e. better) than that of FAAS, mainly due to the longer residence time of atoms in the graphite furnace.

AAS generally requires an individual analysis for each element, and a large filter or several filters are needed to obtain concentrations for all of the elements interested. Airborne particulates are chemically complex and do not easily solubilize completely. Hence, if the sample is not totally digested, the elemental concentration obtained by AAS will not be the total concentration, as

measured by XRF or INAA. AAS is a useful complement to other methods, such as XRF and PIXE, for species such as Be, Na and Mg.

2.2.4 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

In ICP-AES (Fassel and Kniseley, 1974), the extracted/digested aqueous sample is introduced into an argon plasma, consisting of free electrons and ions. The plasma is inductively coupled by a radio frequency (R.F.) field, which oscillates at 27 M Hz or 40 M Hz, through a water-cooled load coil. The load coil surrounds a quartz torch that supports and confines the plasma. In ICP, sample vaporization, atomization and ionization occur at temperatures in excess of 6000°K, raising valence electrons above their normal stable states. When these electrons return to their stable states, photons of light are emitted which are unique to the corresponding excited elements. The emission intensities at specified wavelengths are detected. These intensities are proportional to the concentrations of corresponding elements in the sample. By comparing the emission intensities from known standards, the elemental concentrations in the sample are quantified.

The ICP-AES method is capable of determining a large number of elemental concentrations simultaneously using a small sample volume. It has a larger linear calibration range of 4-6 orders of magnitude. However, its elemental detection capabilities are 10 to 100 folds poorer than that of GFAAS (section 2.2.3), but are comparable with or superior to that of FAAS. Also, there are much more spectral interferences in ICP-AES than in AAS. As with AAS, this method requires complete extraction/digestion and destruction of the sample.

2.2.5 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In ICP-MS (Gray, 1986; Douglas, 1988), an ICP is coupled with a mass spectrometer. An aqueous sample is introduced into the inductively-coupled argon plasma, where it is vaporized, atomized and ionized (see section 2.2.4).

A portion of the ions is introduced through an interface assembly into a differentially pumped mass spectrometer. The interface assembly extracts and focuses the ions into an ion filter (e.g. quadrupole filter). The filter separates ions based on their mass to charge ratios (m/z). Ions exiting the filter are detected by a channel electron multiplier detector. The detector response is captured and processed by computer. The ion counts of elements detected at specified m/z values are proportional to the concentrations of the corresponding elements in the sample. Quantitation is performed using calibration curves derived from known standards.

As with ICP-AES, ICP-MS is capable of determining multi-elements simultaneously and has a larger linear calibration range. The detection limits of ICP-MS are comparable to that of GFAAS; both are 10 to 100 folds lower (i.e. better) than that of ICP-AES. Also, interference in ICP-MS is much less than that in ICP-AES. In addition, ICP-MS has the unique capability to measure isotope ratios. However, similar to ICP-AES and AAS, ICP-MS requires complete extraction/digestion, and hence, destruction of the sample. This may be a problem, if filters can not be sectioned. Otherwise, half of the filter can be analyzed for elements by ICP-MS and other half can be examined for other parameters by other methods, e.g. the water-soluble ions by IC (see section 2.3). Several studies (Jalkanen et al., 1996; Wang et al., 1995) have used ICP-MS to determine the total concentrations of elements in filter particles.

Among ICP-MS, ICP-AES and GFAAS, ICP-MS is generally the most suitable for elemental analyses of airborne particulate matter, because of its low detection limits, wide linear calibration range, multi-element capability and the unique ability to determine the isotope ratios. For the majority of elements, the detection limits of the ICP-MS method are comparable to those obtained from INAA and much lower than those from XRF (Jalkanen et al., 1996). At ARC, ICP-MS methods have been developed to determine the total concentration of

elements in solid environmental samples and in filter particulate samples simultaneous (Wu et al., 1996 and 1997).

2.3 Water-Soluble Ions Analysis

Water-soluble ions refer to chemicals that are soluble in distilled and deionized water at neutral pH and room temperature. The water-soluble portion of airborne particle associates itself with liquid water in the atmosphere when relative humidity increases. Different emission sources may also be distinguished by their soluble and non-soluble fractions (U.S. EPA, 1996b). For example, the water-soluble portion of potassium in airborne particles is more likely associated with the wood or vegetable burnings, while the water-insoluble portion of potassium is more likely associated with soil profiles. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material. Commonly analyzed cations and anions include ammonium, potassium, sodium, calcium, magnesium, chloride, nitrate, sulphate and phosphate.

For ion analyses, a sample or a fraction of filter is extracted in distilled and deionized water (DDW) and then filtered to remove suspended particulate matter prior to analysis. The monoatomic cations can be analyzed by AAS, ICP-AES, ICP-MS (see sections 2.2.3-2.2.5) or ion chromatography (IC). Using separate columns, IC can be used for the separation and analysis of anions or cations (Weiss, 1995).

In IC (Weiss, 1995), a small amount of solution is injected into the system. The solution is then transported to the ion exchange column by an eluent or a solvent system. The ion exchange column contains stationary phase, consisting of a polystyrene resin co-polymerized with divinylbenzene and modified with functional groups. Usually, quaternary ammonium groups are used as the exchange sites for the separation of anions, whereas sulfonate groups are used for the separation of cations. When analyte ions pass through the column, an ion

exchange process occurs between the mobile phase and the stationary phase. The counter ion of an exchange site is replaced by an analyte ion, and the latter is temporarily retained by a fixed charge. The different affinities of each analyte ion towards the stationary phase dictate the separation. After passing through a suppressor unit, in which the background conductance of the eluent is chemically reduced, analyte ions are detected with a conductivity detector. The resulting peak integrals are converted to concentrations using calibration curves derived from solution standards.

An automated IC is usually the preferred method for the analysis of water-soluble ions. Using different columns, IC provides results for several ions (including the polyatomic ions) with a single analysis. It uses a small portion of the filter extract and has low detection limits.

2.4 Particle Size and Shape

Morphological information, together with chemical features of airborne particles, is used to assist the identification of the sources and transport mechanism of airborne particles.

Both optical microscopy and electron microscopy are used to obtain the particle size and shape information. The resolution obtained by the optical microscopy is typically of 1 to 2 μm , not suitable for fine particles. For fine particulate matter ($< 2.5 \mu\text{m}$), a transmission electron microscope (TEM) or a scanning electron microscope (SEM) are used (Schamber, 1993), providing resolution of a few angstroms ($10^{-4} \mu\text{m}$).

The information obtained from the analyses by optical and scanning microscopy is usually considered to be qualitative, due to the limited number of particles counted. To achieve a quantitative analysis, a sufficient number of particles must be properly sized and identified by morphology and/or chemistry to represent the entire sample.

Quantitative analysis is expensive and requires complex technique, a high degree of skills, and extensive quality assurance (U.S. EPA, 1996).

2.5 Recommendations

- (1) The mass, elements and water-soluble ions should be analyzed for PM source profiles for receptor modeling. Morphological information of PM should also be obtained to assist the identification of the sources and transport mechanism.
- (2) For elemental analysis of PM collected on filters, XRF is the most commonly used method. The filter sample analyzed by XRF can be later analyzed by another method such as IC for water-soluble ions. It is often applied together with INAA, AAS or ICP to analyze for elements that are not easily detectable by XRF. If the XRF method is not available or insufficient sample is collected, then ICP-MS is an alternative choice. If both elemental analysis by ICP-MS and analysis of water-soluble ions by IC are required, the filter has to be sectioned. For certain elements, such as zirconium and titanium, the recoveries by ICP-MS are relatively low due to incomplete dissolution of PM samples (Wu et al., 1997).

3. ANALYTICAL METHODOLOGIES FOR ORGANIC MEASUREMENTS

Organic compounds and elemental carbon contribute to visibility degradation and negative health effects on humans. The chemical composition of the organic fraction is not well understood. Many recent studies focused exclusively on these compounds (Wolff et al., 1982; Poster et al., 1995).

3.1 Sample Pretreatment and Storage

Prior to the collection of particulate matter, filters have to be pre-cleaned by solvent extraction or by baking at high temperature (550 C for 24 hours). They are preserved individually in aluminum foil and stored in plastic bags. After sampling, filters are folded and returned to their original packaging. Samples are stored at -20 C immediately after collection, shipped to the lab and

then stored at -20 C. The samples could be stored prior to extraction for up to one month.

3.2 Organic Carbon and Elemental Carbon

The analysis of organic and elemental carbon, based on oxidation of the entire carbon pool, was studied by many investigators (U.S. EPA, 1996). The distinction between the organic compounds and the elemental carbon is critical. There are three methods that are commonly used: thermal/optical reflectance (TOR), thermal/optical transmission (TOT) and thermal manganese oxidation (TMO). In the TOR method, which is recommended by the U.S. EPA, the filters are submitted to volatilization and combustion at temperatures ranging from room temperature to 120, 250, 450 and 550 C in a 100% helium atmosphere; then to combustion at temperatures of 550, 700 and 800 C in a 2% oxygen 98% helium atmosphere. The carbon evolved at each temperature is converted to methane by a methanator and quantified by a flame ionization detector (FID). Organic carbon is defined as that which evolves prior to re-attainment of the original reflectance, and elemental carbon is defined as that which evolves after the original reflectance has been attained. TOT method is similar to TOR but transmission of light is analyzed instead of reflectance from the filter. The TMO method uses manganese dioxide as an oxidizing agent throughout the analysis. Carbon evolved at 525 C is classified as organic carbon and carbon evolved at 850 C is classified as elemental carbon.

In the United States, TOR and TMO are the most widely used. Desert Research Institute (DRI) laboratories developed their own TOR instrument.

A detailed description of the instrument is found in Chow's paper (Chow et al., 1993). Sunset Laboratories are currently manufacturing TOR carbon analyzers.

3.3 Solvent Extraction

3.3.1 Choice of Solvent

The choice of solvent is critical for the analysis of organic compounds. The selection should be based on the nature of the organic compounds to be extracted. The solvents commonly used were dichloromethane (Benner et al., 1990; Poster et al., 1995), benzene (Roussel et al., 1992), acetone (Brorström-Lundén et al., 1994), methanol (Leister and Baker, 1994), hexane (Dannecker et al., 1990). Mixture of solvents were also used such as benzene-methanol (Ciccioli et al., 1993), hexane-benzene-isopropanol (Mazurek et al., 1991; Rogge et al., 1993b).

Polar solvents such as isopropanol and acetone were used to extract efficiently polar compounds from solid matrices. Environment Canada, Downsview laboratories use a mixture of dichloromethane-isopropanol (P. Blanchard, Personal Communication).

3.3.2 Soxhlet Extraction

In this extraction method the extracting solvent boils in a boiling flask of the soxhlet apparatus. After condensation, the solvent drips in a thimble containing the material to be extracted. Once the thimble is filled, the solvent, with the extracted organics, is siphoned to the bottom of the boiling flask. This cycle is repeated for about 24 hours to make sure that all the organics are extracted. After removing the solvent by evaporation, the organics are submitted to quantification and identification.

Soxhlet extraction requires a lengthy extraction time. It is an EPA method for solid matrices (US EPA method 3540). This method is tedious and uses a relatively large amount of solvent. The large glassware used could be the source of contamination as well. This extraction method, with toluene as solvent, is used by Environment Canada Laboratories in Ottawa (Personal Communication, Mylan Tardiff, Ottawa).

3.3.3 Sonication

Sonication bath was also used to extract the organic compounds from the filters using different solvent systems (Rogge et al., 1993b; Mazurek et al., 1991; Leister and Baker, 1994; Dannecker et al., 1990; Poster et al., 1995; Ciccioli et al., 1993).

The sonication was done using a sonibath operating at room temperature for about one hour. It is rapid and efficient in extracting organics adsorbed on the inorganic matrix, since it provides energy to break down the interaction organic-inorganic matters and increases the solubilization capacity of the organic. This method was shown to be the most efficient in extracting organics from soils and sediments (A. Kharrat, unpublished results).

3.3.4 Supercritical Fluid Extraction

This technique extracts organics using a solvent at its supercritical status of pressure and temperature. The material to be extracted is transferred into a stainless steel cell. The cell is flushed with the supercritical fluid. The extractants are trapped on a solid adsorbent. The organics are then flushed out of the trap, using an organic solvent, to a recuperation vial. The extraction was carried out by Lewis for particulates at a temperature of 110 C (Lewis et al., 1995). The solvent used was CO₂ and 10% toluene at 400 atm. for 90 min.

Supercritical fluid extraction does not use a large amount of solvent and it is relatively quick. However, not many investigators have adopted this method because of the cost associated with the purchase of the instrument. ARC Vegreville owns and operates a supercritical fluid extractor with capability of using a solvent modifier that allows usage of different solvent mixtures such as carbon dioxide and methanol.

3.4 Fractionation

Fractionation can be performed without extracting the organics from the solid matrix. It was used to separate non-polar, medium polar and polar

compounds with different solvent system such as cyclohexane, dichloromethane and acetone (Daisey et al., 1982) or solvent change during extraction i.e. hexane, benzene-isopropanol (Gundel et al., 1993).

Fractionation can also be accomplished on a hydrocarbon mixture after extraction from the solid matrix. This protocol uses low pressure liquid chromatography with glass columns (Hannigan et al., 1994) or high pressure liquid chromatography (HPLC) with stainless steel column (Gundel et al., 1993; Brorström-Lundén et al., 1994).

3.5 Detection

Several detection methods were used to analyze organics after extraction from the solid matrix.

3.5.1 Electrobalance

Electrobalance was used to weigh all the organics after extraction or different fractions after fractionation (Daisey et al., 1982). The weighing method does not give any information about the nature of the organics analyzed.

3.5.2 Gas Chromatography

The most used technique for detection and quantification is the gas chromatography (GC) equipped with a detector. This technique consists of injecting the organic mixture of compounds in a hot (~ 300 C) injector, then separating each of the organic compounds based on the difference of their boiling points or on the difference of their polarities and boiling points. Once injected, the organic molecules are eluted inside a column heated in an oven. The column could be packed with a solid absorbent or capillary. The temperature inside the oven could be constant or increased up to a limit of about 400 C. In side a packed column, organic molecules interact with a solid absorbent at the gas phase. In a capillary column, the separation occurs by interaction of the organic molecules with a thin film of polymer coating the

inside of the glass column. A carrier gas is used to enhance the separation and the elution of the organic compounds through the column. To analyze the organic compounds different types of detectors could be used. The most common is the flame ionization detector (FID). Organics are "burned" and form charged entities. A current is produced and measured by two electrodes placed inside the detector. The current is proportional to the amount of organics eluting through the column.

Another type of detector is the mass spectrometer (MSD) (see for example Rounds et al., 1993). It is based on detecting charged fragments of organics after bombardment by an ionizing beam. This detector allows quantification and accurate identification of organic compounds separated by gas chromatography.

The third type of detector which is commonly used is the electron capture detector (ECD) (Leister and Baker, 1994) specific for analysis of halogenated organics.

Gas chromatography equipped with capillary columns is a well recognized method to be very efficient in separating organic compounds. When the chromatographs are equipped with an autosampler, the process of a large number of samples becomes possible. Data are collected and processed with computers. Mass spectrometers are usually interfaced with a mass spectrometer library to allow matching of the compound being analyzed with compounds which mass spectrum previously stored. This allows a rapid identification of target and non-target compounds.

Alkanes and PAHs are usually identified with a low resolution mass spectrometry (when analyzing PAHs, Selective Ion Mode , SIM, is used). However, PCB and dioxins are usually identified with a high resolution mass spectrometry because of the increased sensitivity and selectivity, and certainty of results.

3.5.3 Liquid Chromatography

The principles of the high-performance liquid chromatography (HPLC) are similar to the ion chromatography with the exception of the column. HPLC uses packing such as silica or alumina capable of separating organic compounds; the separation is based on the polarity of the molecules to separate. To enhance the separation capabilities of the HPLC technique different solvents with different polarity are used. The most common detector is the UV detector with constant wavelength or with a diode array. Other detectors used include refraction index, fluorescence and electrochemical detectors. In particulate matter studies, it was found in the literature that the organic mixture was separated into 3 fractions: low polarity, medium polarity and high polarity fractions (Sheffield et al., 1994). This technique is also used to analyze PAHs (Roussel et al., 1992). The disadvantage of this method is that all PAHs are not well separated. The use of HPLC to fractionate the organic fraction is a documented method. A method developed in our laboratory is already in use to fractionate organics into alkanes, PAHs, O- and N-PAHs, phenol and acid fractions.

3.5.4 Infrared Spectroscopy

The infrared spectroscopy (IR) technique consists of illuminating organic molecules by an infrared beam with a wavelength changing from 2.5 to 15 microns. The organic molecules absorb energy at different wavelengths depending on the nature of the bonds (CH, CO, CC etc.) existing within the molecules. Fourier Transform Infrared Spectroscopy (FTIR) allows a lower detection limit and increase of confidence in the interpretation of the results. The infrared technique was mostly used to determine the functionality of different compounds, i.e. acids, aldehydes, alcohols, phenols, esters, quinones and amines (Gundel et al., 1993). This technique is not used to identify specific compounds,

unless it is coupled with GC. Unfortunately, GC-FTIR is not as accurate as other methods.

3.6 Recommendations

For the analysis of organic compounds, we recommend the following:

- (1) The solvent has to be polar in order to allow a maximum extraction efficiency of all organics. Dichloromethane or dichloromethane-isopropanol is the solvent to consider.
- (2) Extraction technique recommended is the sonication method. It is efficient for extracting polar compounds. It is fast, cheap and not labor intensive.
- (3) Fractionation using HPLC column is preferred.
- (4) The detection method of choice is the gas chromatography coupled with mass spectrometry.

PART II

SOURCE APPORTIONMENT STUDIES

4. SOURCE PROFILES FROM LITERATURE

Source apportionment requires ambient data as well as source emission profiles. In Alberta, two stations are currently collecting ambient PM data, one is downtown Edmonton and the second is in downtown Calgary. In most of the source apportionment studies the source profiles were taken from the literature with recognition that these profiles do not necessarily represent the location. Secondary particulates are shown in some studies to have a large contribution to ambient particulate matter. A brief description of their formation is presented.

4.1 List of the Databases

The databases for PM source profiles collected prior to the writing of this report are listed below:

- (1) US Environmental Protection Agency SPECIATE Database: The database is located in the internet at this following address: <http://www.epa.gov/ttnchie1/software.html#speciate>. Species concentration and uncertainty was reported to the four fractions: 0-2.5 μm , 2.5-10 μm , 0-10 μm and total. This database is updated regularly and the latest version was completed in 1993.
- (2) Desert Research Institute: The DRI database was kindly given to us by electronic mail. It contains profiles from about 100 sources, mostly area sources. No rating was attributed to the profiles.
- (3) California Air Resources Board: This database contains 27 profiles from dust resuspended sources and 13 profiles from point and non-resuspended area source for 4 fraction size, PM_{10} , $\text{PM}_{2.5}$, PM_{10} and TSP. This database was compiled in 1989.
- (4) Pacific Northwest source profile library includes eighty sources in Oregon, Washington and Idaho. Profiles from point sources, area

sources, diesel and leaded autos and fugitive dust sources are described. This database was also compiled in 1989.

- (5) Journal Articles: many journal articles were collected.

4.2 Profile Format

In the EPA SPECIATE database, composition data are generally reported for four size range: 0-2.5 μm , 2.5-10 μm , 0-10 μm and total suspended particles (0-35 μm). The size interval of PM_{10} (0-10 μm) was calculated from the data of 0-2.5 and 2.5-10 μm .

Each profile is associated with entries to describe the nature of the profile. Beside the NAME and the NUMBER of the profile. The DATA SOURCE entry contains description of the sampling technique and the analytical methodology used. The CONTROL DEVICE entry states whether or not the point source is equipped with any type of particulate matter emission control, such as electrostatic precipitator. The DATA QUALITY entry presents rating to the quality of the profile. The significance of each rate (A, B, C, D or E) is presented as following (U.S. EPA, 1990):

Quality A: Composition and mass fraction data obtained for the size intervals 0-2.5 μm , 2.5-10 μm and total particulate measured for several sources using sound sampling and analytical methodologies. Profiles are considered representative and recommended for use.

Quality B: Composition and mass fraction data obtained for the size intervals 2.5 μm , 2.5-10 μm and total particulate measured for a few sources using generally sound methodology.

Quality C: Composition data obtained for size intervals 0-2.5 μm , 2.5-10 μm and total particulate measured from few sources using a generally sound methodology and mass fraction data obtained of below average quality; or composition data obtained for two of the three size intervals 0-2.5 μm , 2.5-10 μm and particulate measured from a large

number of sources using sound methodology coupled with mass fraction data of below average quality.

Quality D: Composition data from limited number of sources using uncertain or undocumented methodology with mass fraction data below average quality (or sound/poor).

Quality E: Composition obtained from a single source with poorly documented methodology coupled with mass fraction data of poor quality. Use profiles E only if there is no other information.

5. SECONDARY PARTICULATES

5.1 Origin and Mode of Formation

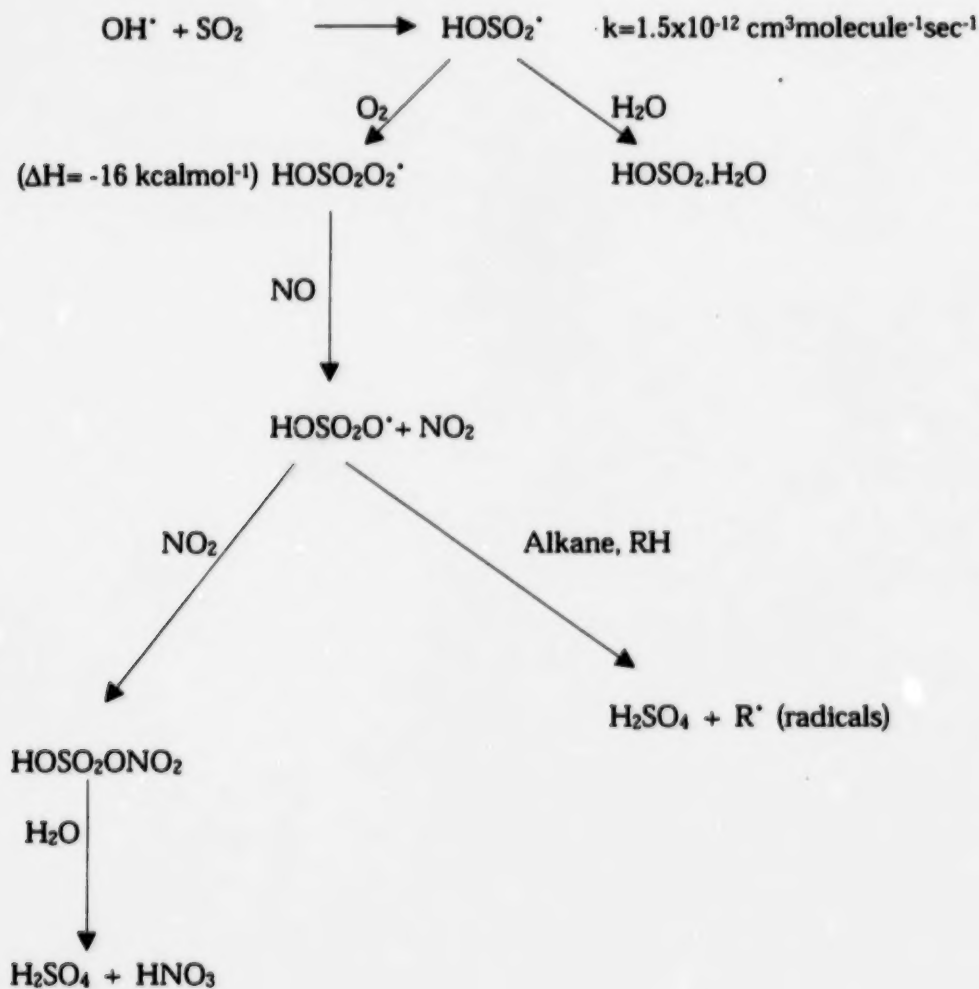
Secondary particulates are the products of chemical reactions taking place in the atmosphere. These reactions can be initiated in the gas phase between gas molecules, or between gas molecules and already existing particles. The smallest particles ($<0.05\ \mu\text{m}$) have a lifetime on the order of several minutes before they coagulate with other particles to form larger ones. Because they are constantly formed during the day time, by reactions initiated with the sun light, their concentration in the atmosphere reaches a steady state and declines during night time. The larger particulates ($0.05\text{-}1\ \mu\text{m}$) have a longer lifetime, usually on the order of several hours to days (Davies, 1974; Fennelly, 1975).

The formation of secondary particulate matter requires the presence of chemicals such as SO_2 , NH_3 , NO_2 , water and hydrocarbons as well as sunlight and ozone. These chemicals originate from both natural sources and anthropogenic (man-made) sources. Natural sources include oceans, volcanoes, soil surfaces as well as trees, vegetations and decaying organic matter. The man-made sources include combustion systems, vehicle emissions and industrial processes.

Secondary particulates are found in both rural and urban areas. They are classified in the following classes: sulfates, nitrates and organics.

5.1.1 Particulate Sulfates

The primary ingredient of sulfate particles is sulfuric acid which could be formed through different pathways (Seinfeld, 1980):



In the atmosphere, sulfuric acid droplets react with ammonia or metal oxides to form sulfate salts, such as:



This reaction is usually instantaneous and the limiting step is the transformation of SO_2 to H_2SO_4 .

5.1.2 Particulate Nitrates

The precursor of nitrate particulate matter is nitric acid (HNO_3). It is produced in the atmosphere following this series of reaction:



Nitric acid could also be resulting from the reaction of NO_2 with hydroxy radicals



The subsequent reaction of nitric acid with ammonia leads to the formation of ammonium nitrate:



5.1.3 Particulate Hydrocarbons

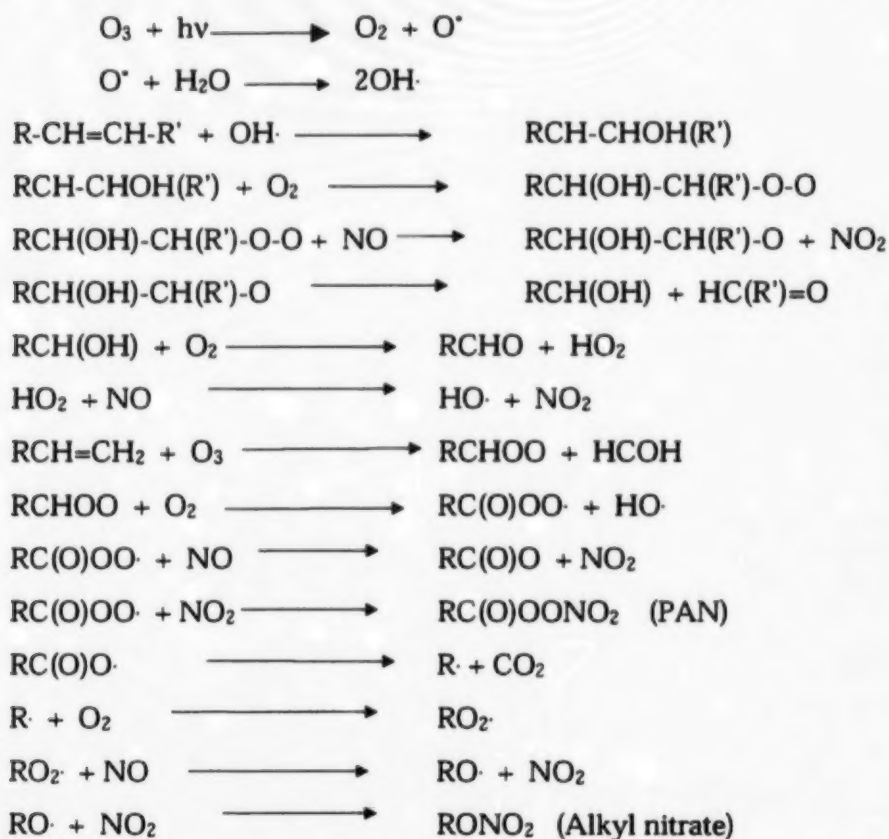
Hydrocarbons are highly reactive in the atmosphere. Their lifetimes due to the reaction with hydroxy radical and ozone were evaluated to be relatively short except for low carbon number alkanes, Table 1.

Table 1. Lifetimes of VOCs in the troposphere.

VOC	Reaction with OH ^a	Reaction with ozone ^b
Methane	12 years	> 4,500 year
Propane	13 days	> 4,400 years
Propene	7.0 hours	1.5 days
Isoprene	1.8 hours	1.2 days
α -Pinene	3.4 hours	4.6 hours
β -Pinene	2.3 hours	1.1 days

^a Prinn et al., 1987. ^b Logan, 1985.

Hydrocarbons are efficient absorbers of UV, visible and IR radiations. In the troposphere, a complex chain reaction, initiated by ozone and sunlight, leads to the formation of hydroxyl radical, OH $\cdot$, and consequently to the destruction of organic compounds (Fergusson 1982; Finlayson-Pitts 1986; Wayne 1985). The followings are few examples:



Nitrogen dioxide (NO₂), formed during the decomposition of hydrocarbons by different paths, reacts with hydroxyl radical, OH, and produce nitric acid.

Intermediate peroxide radicals combine together and produce large organic molecules to form solid particulates. These particulates may remain pure organic entity, react with other gas molecules or condense with liquid droplets.

The following table summarizes the amount particulate matter as well as NO_x, SO_x and hydrocarbons that contribute to the formation of secondary particulates in Alberta.

Table 2. Emission in Alberta (ktonnes)

	Anthropogenic sources	Open/biogenic sources
VOCs	630	1550
NO _x	500	1.5
SO ₂	600	0
PM	200	15,000

Source: Canadian Emissions Inventory of Criteria Air Contaminants (1990).

The secondary nitrate and sulfate particulates are measured with the ambient particulates. The difference between the ambient concentration and the concentration attributed to all the sources is considered the amount of secondary particulates. The emission of VOCs, NO_x and SO₂, precursors of secondary particulates, in Alberta is considerably higher than that of PM. Therefore, it is expected to find substantial amounts of secondary particulates in the ambient particulates. The secondary hydrocarbon particulates could be calculated from the ratios of organic carbon/elemental carbon (OC/EC) found in the sources and

in ambient air. These ratios are expected to be sensitive to diurnal and seasonal variations (Turpin et al., 1991).

5.2 Abundance

In the 1984 particulate matter study completed by Environment Canada (Environment Canada, 1984) for all the Canadian provinces, only sulfates were reported as secondary particulates. It was found that they contribute to 1.5 and 14% for the coarse and the fine fractions respectively. In the REVEAL study (Lowenthal et al., 1997), British Columbia, secondary sulfates and secondary nitrates were reported to represent 25% and 27% in the fine fraction.

In the San Joaquin, California, valley study Chow et al. (Chow et al., 1992) reported 6-11% of sulfate particulate matter and 56-79% nitrate particulate matter in the atmosphere for the coarse fraction. In a more recent study in San Jose, California, Chow et al. (1995) reported that the percentages of secondary sulfates and secondary nitrates were 3% and 18% of the ambient concentration of coarse fraction (PM₁₀).

Turpin et al. reported the secondary particulate concentrations for organics were in the range of 16 to 62% of the total organic carbon concentration (Turpin et al., 1991).

6. ALBERTA INFORMATION

6.1 Alberta Sources

Environment Canada (Environment Canada, 1993b) surveyed all the major sources, in Canada, emitters of particulates, SO₂, NO_x and volatile organic compounds (VOCs). Table 3 summarizes the value for each type of pollutant by sector for the province of Alberta.

Table 3. Major Emission Sources for PM, SO₂, NO_x and VOCs in Alberta

	Emissions in Tonnes per Year			
	PM	SO ₂	NO _x	VOCs
Industrial Processes				
Asphalt Production	3,225			
Bakeries				348
Cement and concrete manufacture	8,499	294	4,908	
Coal industry	20,006	2,753	159	337
Crude oil production		51,200		
Ferrous foundries	45		2	2
Grain industries	10,677			
Mining and rock quarrying	264			
Natural gas processing	474	237,505	96,687	2,371
Oil sands	4,149	148,211	15,855	32
Other chemicals	2,460	245	9,640	2,218
Petroleum industry	188	1,277	8,090	5,482
Petroleum refining	760	7,078	5,737	6,244
Plastics & synthetic resins fabrication				1,483
Pulp and paper industry	2,179	1,212	301	1,414
Upstream oil & gas operations				437,279
Wood industry	29,794	3	1,674	1,752
Other industries	4,349	3,727	34,342	184
Fuel combustion				
Commercial fuel combustion	265	379	4,329	164
Electrical power generation	81,731	101,629	87,935	877
Residential fuel combustion	1,011	492	5,757	672

Table 3. (Cont'd)

	Emissions in Tonnes per Year			
	PM	SO ₂	NO _x	VOC
Residential fuelwood combustion	453	5	37	1,804
Transportation				
Aircraft	146	198	2,770	1,021
Heavy-duty diesel vehicles	4,141	3,666	51,802	5,838
Heavy-duty gasoline trucks	31	25	2,320	2,130
Light-duty diesel trucks	15	287	365	254
Light-duty diesel vehicles	7	125	136	48
Light-duty gasoline trucks	174	482	16,346	24,284
Light-duty gasoline vehicles	314	688	30,847	46,603
Marine		8	15	2,229
Motor cycles	2	2	67	333
Off-road use of diesel	5,652	3,178	58,106	6,509
Off-road use of gasoline	806	303	13,170	17,760
Railroads	1,761	1,371	32,637	1,585
Tire wear	4,914			96
Incineration				
Wood waste incineration	880	15	152	1,668
Other incineration	10	157	193	228
Miscellaneous				
Application of surface coating				4,724
Cigarette smoking	297			
Dry cleaning				1,242
Fuel marketing				10,227
General solvent use				41,172
Pesticide and fertilizer application	4,734			8,211
Structural fire	36		13	46
Totals	194,448	566,515	486,713	637,653

6.2 PM Related Studies in Alberta

In Alberta, few studies have been conducted or are currently ongoing dealing with the assessment of particulate matter.

- (1) Environment Canada is conducting measurement of particulate matter in Esther area. Results are yet to be generated.
- (2) The West Central Airshed Study which deals with the acidity and deposition of PM. Species characterization data is very limited (E. Peake, Personal Communication) and results have not been published.
- (3) A study entitled "Investigations of Flare gas Emissions in Alberta" was conducted by M. Strosher of Alberta Research Council. The purpose of the study was to assess the emission of organic compounds from flares. Collection of particulate was done on glass fiber filters and analyses were conducted mainly for mono- and polyaromatic hydrocarbons (Strocher, 1996).
- (4) Dr. F. Goodarzi from Energy Mine and Resources, Calgary, is currently conducting a study with power generating companies on particulate matter analysis. The results are however still confidential (F. Goodarzi, Personal Communication).
- (5) A study was conducted in 1994 by Inland Cement, in association with HBT Agra Ltd., Clean Air Engineering, Alberta Environmental Centre and Environmental Quality Management Inc. dealing with the determination of the Electrostatic Precipitator efficiency (Environmental Quality Management, 1994). Particulates were collected and analyzed for metal species content. Ten elements were analyzed.
- (6) TransAlta is conducting a study on particulate matter in conjunction with CANMET. The results of the ongoing study are

still confidential (Ingrid Liepa, TransAlta, Personal Communication).

7. SOURCE APPORTIONMENT

7.1 Review of the Existing Methods

Source emission profiles (SEP) are commonly composed of a reasonably large number of chemical species, each having its own statistical attributes, e.g. mean, variance, and probability density function. Commonly there are several of these species which are correlated, thus complicating interpretation from individual analyses. The latter presents the need for some sort of multivariate statistical treatment which can utilize the covariance among 2 or more variables measured on the same subject/unit. The most commonly used multivariate methods used for fitting SEP data to any model are factor analysis, principal components analysis and multiple regression. For discussion purposes, the first two can be considered as one, most often referred to as factor analysis (differences are mostly related to axis rotation algorithms). The latter utilizes weighted, least squares, in which mean concentration of chemical species is weighted by its standard deviation, i.e. uncertainty (Hopke, 1985; Watson et al., 1984; Pace and Watson, 1987).

7.1.1 Factor Analysis

Factor analysis has been applied in air pollution studies since the mid-1960s (Hopke, 1985). The method remains useful for these types of data matrices because of its utility for reducing the data dimensions of a problem and guiding the user to identifying 'factors' (profiles) having 'loadings' represented by coefficients of the original variables (chemical species) associated with each factor. For example, a factor might be identified, in the current context, as 'road

dust' because silica has a high loading on factor 1, but factor 2 could best described (by the user's judgment) as a 'Portland cement' factor having high loadings by aluminum and calcium, but factor 3 is called a 'biogenic' factor due to high a loading by organic carbon. If our study had gathered data on 15 chemical species, we would then have this large collection of variables (species), high dimension, reduced to only 3 factors which contain all the original variance of the 15 original variables or species. Hence, a reduction in dimension and the factors (profiles) are independent or orthogonal to one another. This approach is statistically sound, and is useful for identifying inconsistent data, but depends on (1) the objectives of the sampling, (2) requires, by some accounts, at least 5-10 times the number of samples as you have species, (3) data must be present for each species in each sample, otherwise a sample is omitted due to problems encountered during matrix operations, and (4) if meteorology is a major component at a location, it has been shown that collocated samplers cannot be separated by factor analysis techniques (see Hopke, 1985, chap. 7).

7.1.2 Chemical Mass Balance (CMB)

Work in the late 1960s and early '70s at the University of Oregon's Graduate Center (Beaverton) led to the development of a least squares, multiple regression approach to particulate matter apportionment, which led to adoption of the phrase 'chemical mass balance', from the earlier one, 'chemical element balance' (CEB). This was led by Cooper and Watson (1980), and later Watson, the latter having published his Ph.D. dissertation topic (Watson, 1979) which focused on developing the methods for analyzing particulate matter still in use, with minor refinements. Extensive work related to the validation of the CMB was done in the early eighties and published (Hopke, 1985).

CMB methodology assumes some knowledge about the kinds and numbers of point sources (Pace and Watson, 1984). Therefore, ideally the airshed is first characterized. A review of the literature clearly shows that for many

projects, researchers rely upon database libraries and/or published emission profiles in place of actual data for a given airshed.

Strength of the CMB model approach comes from (1) the fact that it has been in use for almost 20 years and a large reservoir of results from many studies apparently supports its utility, (2) it is unique in that it incorporates the uncertainty in both the ambient data and the emission source data developed by Watson et al. (1984), and (3) large databases of source profiles (DESERT) are now available from the Desert Research Institute, Reno, NV (John Watson is resident there and first author of the current software code [Watson et al., 1997]) and the US EPA (database named SPECIATE).

The assumptions (Pace and Watson, 1984) that should be met when applying the CMB model are:

- (1) Compositions of source emissions are constant over the period of ambient and source modeling.
- (2) Chemical species do not react with each other, i.e. they add linearly.
- (3) All sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized.
- (4) The number of sources or source categories is less than the number of species.
- (5) The source compositions are linearly independent of each other.
- (6) Measurement uncertainties are random, uncorrelated and normally distributed.

Pace and Watson (1984) point out that violating the above can have very negative impacts on interpretation of conclusions and therefore the user should be very careful to combine the results with good expert judgment and validate according to published guidelines.

John Watson, at DRI (Personal Communication, September 3, 1997). emphasizes these points: (1) the CMB is best suited for supplementing other statistical tools for 'pattern recognition', e.g. combining it with bivariate and multivariate analyses, like principal components/factor analysis, (2) the CMB and all dispersion models are useless for monitoring when dead, stale air builds up, because they are dependent upon meteorology for mixing, (3) CMB is good for identifying categories of emissions so that more detailed studies can zoom in on specific chemicals, (4) CMB helps characterize seasonal variation, (5) it is a good precursor tool so that dispersion models can be selected or built which are customized to specific emission sources and (6) reliability and better sensitivities are met by insuring that the chemical species having the most precise estimates are weighted most heavily and assumptions of the model are met (Watson et al., 1984; Lowenthal, 1997).

The above underline one thing the CMB model approach is not, it is not a monitoring tool in the truest sense because it is intended to help identify major sources in mixtures (John Watson, Personal Communication, September 3, 1997). But, it can be valuable for designing monitoring networks where each station is designed to best quantify a given emission source. And, the CMB method does not yield a unique solution, i.e. the solutions to the linear equations are dependent upon very careful selection of source emission libraries, given that actual emissions data for a local airshed are not used (Lowenthal, 1997, and references therein).

7.2 Application of the CMB Modelling

7.2.1 Canadian Studies

This section summarizes several Canadian studies conducted in relation to CMB modelling.

7.2.1.1 Summary of a report for Environment Canada on, 'inhalable particulates' prepared by, the Environmental Applications Group Ltd. (1984) Toronto .

- (1) Seven urban areas in Canada were included in a study by the Environmental Applications Group Ltd., (Environment Canada, 1984), for the period, August 22, 1983 through January 14, 1984, using data from coarse (2.5 – 15 μm) and fine (<2.5 μm) particulates:
 - Halifax
 - Montreal
 - Ottawa
 - Toronto
 - Winnipeg
 - Edmonton
 - Vancouver
- (2) Seasonal trends were detected and thus data entered into analyses should reflect this effect.
- (3) Bivariate plots, correlations and regression slopes detected significant relationships between some chemical species suggesting common sources, e.g. Si:Al (crustal dust) and Br:Pb (automobiles and lead smelters) and Mn:Pb (automobile, fuels & additives [MMT]).
- (4) The study opted out of obtaining local source emission data and relied upon data libraries and published reports. They did, however, acknowledge the uncertainty introduced by relying upon non-local data. Apportionment was done by the chemical mass balance (CMB) method highlighted in our report.
- (5) Conclusions from the CMB analyses: (1) CMB was thought to best describe the emissions from road dust, transportation and secondary sulphate; the sources were consistent and uniform across

Canada; (2) using data from profile libraries outside the airshed introduced another source of uncertainty that could be reduced by collecting samples from the target airshed; (3) CMB data quality/confidence was ranked for the 7 cities, Edmonton was 6th in confidence for the coarse fraction and tied with Winnipeg for 2nd in confidence in CMB results for the fine fraction particulates.

The results for Edmonton chemical mass balance are shown in the following charts, Figure 4 and 5.

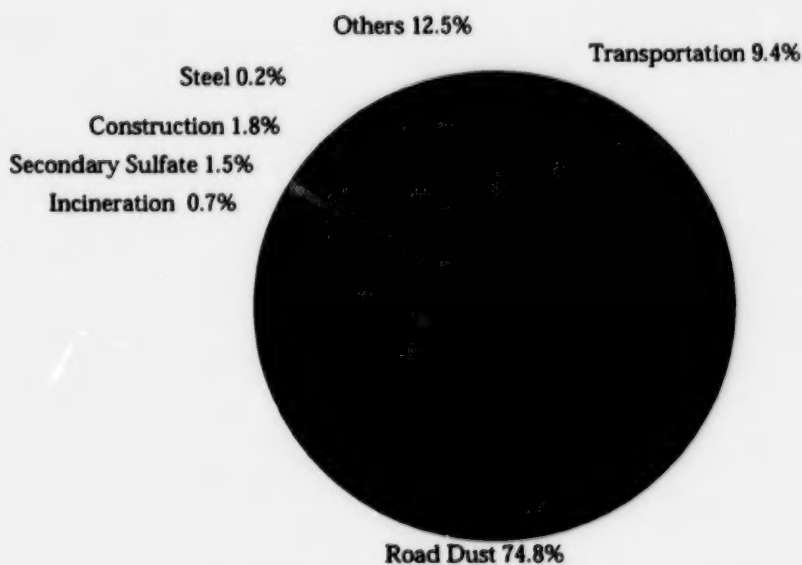


Figure 4. Distribution of PM₁₀ within the city of Edmonton.

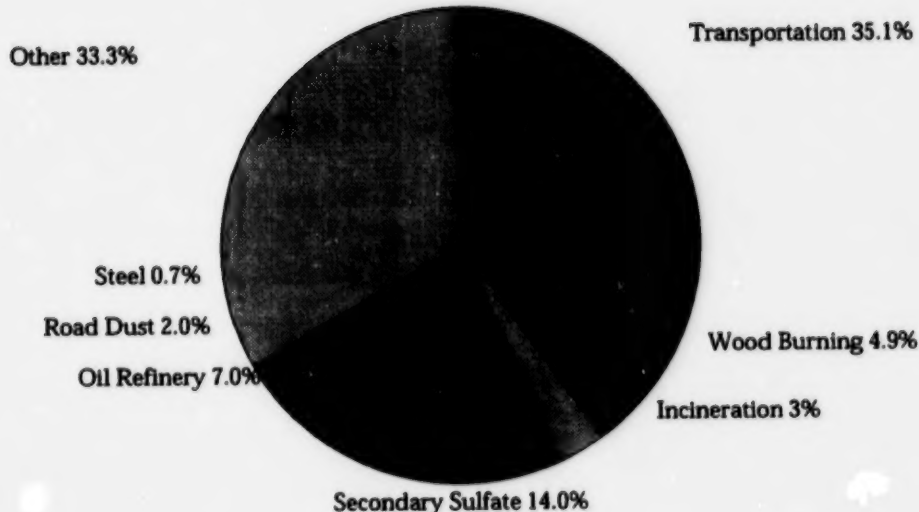


Figure 5. Distribution of PM_{2.5} within the city of Edmonton.

- (6) Recommendations: (1) local airshed data should be gathered in Canadian cities for heavy fuel oil combustion, oil refining, glass manufacturing and incineration to improve source apportionment and reduce reliance upon external profiles; (2-4) the remaining recommendations dealt mainly with physical sampling and analytical technologies, not math-stat procedures.

7.2.1.2 Summary of a report prepared for the Atmospheric Science Expert Panel of the Industry/Government Joint "Sulphur in Gasoline Studies" by Douglas Lowenthal, DRI, Reno, NV (February 1997), entitled, "Motor Vehicle contribution to PM_{2.5} Aerosol in Canadian Urban Areas".

- (1) This report by Lowenthal is a review of Canadian and US studies for the above expert panel.

- (2) Five Canadian studies were reviewed:
- Environmental Applications Group, EAG [above] (1984); CMB model.
 - Lowenthal et al. [REVEAL] (1997); CMB model.
 - Pryor and Steyn [REVEAL] (1994); factor analysis.
 - Lang et al. (1995); CMB versus climatological regional dispersion model (CRDM).
 - Brook et al. (1996); TSP, PM_{10} and $PM_{2.5}$ aerosol concentrations measured but did not directly address vehicle emission sources.
- (3) Conclusions: the EAG studies were consistent in their apportionment of vehicle emissions for Vancouver at 40% of $PM_{2.5}$ and appeared to confirm the apportionment to the other Canadian cities, ranging from 9 to 39% of $PM_{2.5}$. Factor analysis in REVEAL was qualitatively consistent but not quantitatively, 27% of $PM_{2.5}$ to Pitt Meadows near Vancouver. Lang et al. (1995) showed that CMB and the dispersion model showed that the methods could differ by as much as two orders of magnitude; predictions in reductions of ambient PM_{10} were thus dependent upon which method was used.

7.2.1.3 CMB source apportionment during REVEAL by Lowenthal et al. (1994)

The REVEAL study was conducted in the lower mainland of British Columbia. The results of CMB source apportionment for $PM_{2.5}$ are presented in Figures 6 and 7.

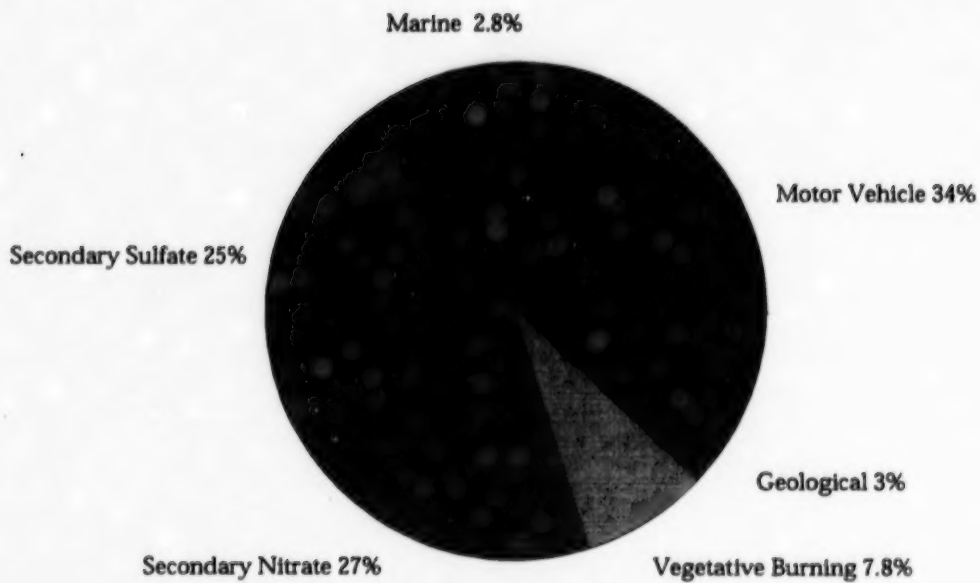


Figure 6. Distribution of PM_{2.5} at Chilliwack.

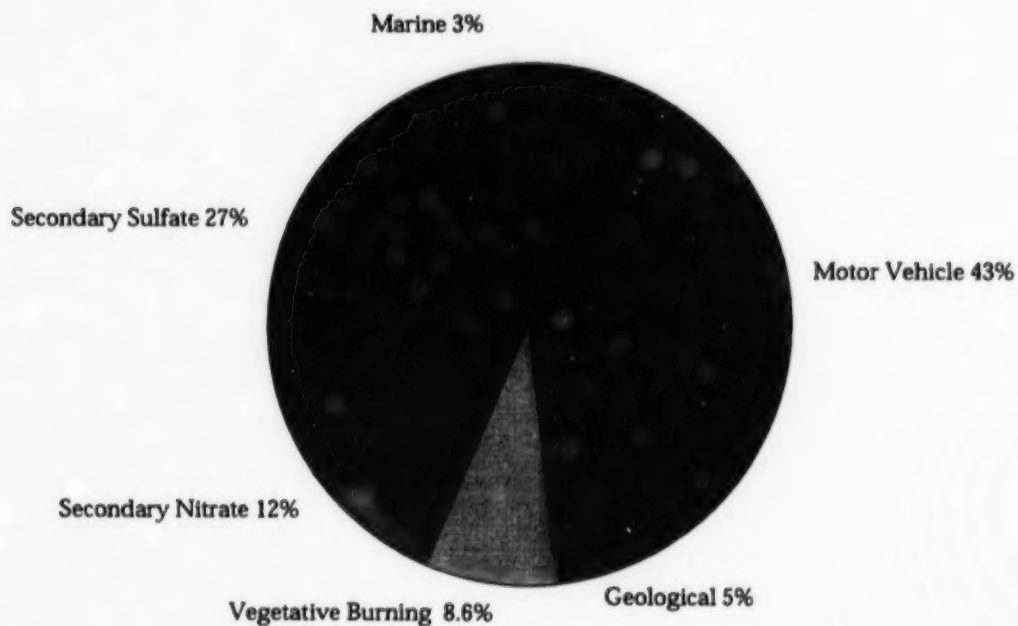


Figure 7. Distribution of PM_{2.5} at Pitt Meadows.

7.2.2 OTHER STUDIES

In the literature, many source apportionment studies were found. The intent here is to present the results of the major sources contributing to the ambient PM₁₀ and PM_{2.5} in locations outside Canada.

The following abbreviations were used:

CMB	Chemical Mass Balance
SPCA	Standard Principle Component Analysis
APCSRM	Absolute Principle Component Scores and Regression Modeling
PCA	Principle Component Analysis
LRA	Linear Regression Analysis

The results are compiled in Tables 4 and 5.

Table 4: Source apportionment results for PM₁₀ outside Canada

Study Location	Statistical Tool	Source Apportionment Results	Reference	Comments
Fourth St. Site in San Jose, California	CMB Receptor Model	Residential Wood Combustion 44%, Road dust 18%, Amm. Nit. 18%, Motor Veh 13%, Amm. Sul 3%, Marine 1%, Unexplained 3%	Fig 5a Chow et al., 1995	
San Carlos St. Site in San Jose, California.	CMB Receptor Model	Residential Wood Combustion 46%, Road dust 17%, Amm. Nit. 19%, Motor Veh 13%, Amm. Sul 3%, Marine 1%, Unexplained 2%	Fig 5b Chow et al., 1995	
Bay Area Air Quality Management District, California	CMB Receptor Model	Paved Road Dust 50%, Constr./Demolition 13%, RWC 11%, Petroleum Processes 6%, On-Road Vehicles 6%, Off-Road Vehicles 2%, Gas Oil Heating 2%, Accidental Fires 1%, Farming Operations 1%, Other sources 10%	Fig 2a Chow et al., 1995	
Rubidoux, California	CMB Receptor Model	Primary Geological 52%, Sec Ammonium Nitrate 23%, Primary Mobile 11%, Sec Ammonium Sulfate 6%, Primary Lime 6%, Marine 2%	Fig 5 Chow et al., 1992a	1988 annual average

Downtown Los Angeles, California	CMB Receptor Model	Crustal 43.4%, Motor vehicles 25.6%, Ammonium Nitrate 17.3%, Ammonium Sulfate 9.4%, Marine 3%	Table 4 Kao & Friedlander, 1995	
Bakersfield, San Joaquin Valley, California.	CMB Receptor Model	Amm Nit. 27%, Geol. 26%, Mot. Veh. 12%, Veg. Burn 7%, Amm. Sul. 7%, Crude Oil 2%, Constr. 1%, Marine 1%, Unexpl. 18%	Fig 4 Chow et al., 1992b	First Quarter Average Source Contributions to PM ₁₀
Bakersfield, San Joaquin Valley, California.	CMB Receptor Model	Amm Nit. 3%, Geol. 73%, Mot. Veh. 7%, Veg. Burn 5%, Amm. Sul. 7%, Constr. 3%, Marine 2%	Fig 4 Chow et al., 1992b	Second Quarter Average Source Contributions to PM ₁₀
Bakersfield, San Joaquin Valley, California.	CMB Receptor Model	Amm Nit. 1%, Geol. 70%, Mot. Veh. 6%, Veg. Burn 8%, Amm. Sul. 6%, Constr. 2%, Marine 2%, Unexpl. 5%	Fig 4 Chow et al., 1992b	Third Quarter Average Source Contributions to PM ₁₀
Bakersfield, San Joaquin Valley, California.	CMB Receptor Model	Amm Nit. 23%, Geol. 43%, Mot. Veh. 10%, Veg. Burn 8%, Amm. Sul. 7%, Crude Oil 1%, Constr. 1%, Marine 2%, Unexpl. 4%	Fig 4 Chow et al., 1992b	Fourth Quarter Average Source Contributions to PM ₁₀
Stockton, San Joaquin Valley, California.	CMB Receptor Model	Amm. Nit 42%, Mot. Veh. 16%, Geol. 13%, Veg. Burn 5%, Amm. Sul. 4%, Unexpl. 21%	Fig 5 Chow et al., 1992b	Source Contributions to 24-Hour PM ₁₀ on 12/11/88
Fresno, San Joaquin Valley, California.	CMB Receptor Model	Amm. Nit 50%, Mot. Veh. 26%, Constr. 10%, Geol. 3%, Veg. Burn 6%, Amm. Sul. 6%	Fig 5 Chow et al., 1992b	Source Contributions to 24-Hour PM ₁₀ on 12/11/88
Fellows, San Joaquin Valley, California.	CMB Receptor Model	Amm. Nit 50%, Crude Oil 16%, Geol. 15%, Amm. Sul. 7%, Veg. Burn 5%, Mot. Veh. 3%, Sec. Org. 3%, Constr. 2%	Fig 5 Chow et al., 1992b	Source Contributions to 24-Hour PM ₁₀ on 12/11/88
Bakersfield, San Joaquin Valley, California.	CMB Receptor Model	Amm. Nit 34%, Geol. 24%, Mot. Veh. 11%, Veg. Burn 5%, Amm. Sul. 5%, Crude Oil 2%, Constr. 1%, Marine 0%	Fig 5 (B) Chow et al. 1992b	Source Contributions to 24-Hour PM ₁₀ on 12/11/88
Lennox, California	CMB Receptor Model	Read Dust 20%, Amm. Nit. 17%, Amm. Sul. 16%, Sec. Carbon 16%, Read Dust 14%, Diesel, 8%, Marine 7%, Gas	Fig 1a Gray et al., 1988	

		1%, Unexplained 1%		
Rubidoux, California	CMB Receptor Model	Read Dust 47%, Amm. Nit. 24%, Amm. Sul. 7%, Sec. Carbon 7%, Diesel 6%, Lime 5%, Soil Dust 2%, Gas 1%, Marine 1%	Fig 1b Gray et al., 1988	
Houston, Texas	CMB Receptor Model	Crustal 62%, Other carbon 5%, Sulfate and Cations 3%, Nitrate 3%, Vehicle exhaust 2%, Marine 1%, Steel 1%, Other 23%	Fig 2a Stevens & Pace, 1984	PM _{2.5} - PM ₁₅
Detroit, Michigan	Factor Analysis Receptor Model	Crustal 63%, Motor Vehicles 16%, Iron and Steel 12%, Organic Carbon 6%, Unidentified 3%	Fig 3a Wolff and Korsog, 1985	PM _{2.5} - PM ₁₅
Olifantsfontein, South Africa	CMB Receptor Model	Domestic Coal Combustion 39%, Sec Amm. Sul. 23%, Power Station Fly Ash 13%, Fugitive Soil Dust 12%, Sec Amm. Nit. 8%, Iron Arc Furnace 3%, Petrol Vehicle Emissions 2%	Fig 1 Reddy et al., 1997	Period June 23 to 30, 1995 PM ₁₀ Conc. 102.6 µg/m ³
Vereeniging, South Africa	CMB Receptor Model	Domestic Coal Combustion 23%, Sec Amm. Sul. 18%, Fugitive Soil Dust 21%, Sec Amm. Sul. 18%, Iron Arc Furnace 15%, Power Station Fly Ash 8%, Sinter Plant Emissions 6%, Sec Amm. Nit. 4%, Vehicle Emissions 2%, Fe-Mn plant emissions <1%	Fig 2 Reddy et al., 1997	Period April 22/94 to April 21/95 PM ₁₀ Conc. 70 µg/m ³
Vanderbijlpark, South Africa	CMB Receptor Model	Domestic Coal Combustion 25%, Fugitive Soil Dust 22%, Sec Amm. Sul. 19%, Iron Arc Furnace 14%, Sinter Plant Emissions 7%, Sec Amm. Nit. 5%, Power Station Fly Ash 5%, Coking Furnace emissions 2%, Vehicle Emissions 1%	Fig 2 Reddy et al., 1997	Period April 22/94 to April 21/95 PM ₁₀ Conc. 58 µg/m ³
Sasolburg, South Africa	CMB Receptor	Domestic Coal Combustion 22%, Sec	Fig 2 Reddy et al.,	Period April 22/94 to April

	Model	Amm. Sul. 21%, Fugitive Soil Dust 20%, Power Station Fly Ash 13%, Iron Arc Furnace 10%, Sec Amm. Nit. 7%, Sinter Plant Emissions 5%, Coking Furnace emissions 1%, Fe-Mn plant emissions <1%	1997	21/95 PM ₁₀ Conc. 57 µg/m ³
Kohler Industries in Nelspruit, South Africa	CMB Receptor Model	Biomass burning emissions 40%, Fugitive soil dust 18%, Sec. Amm. Bisul. 15%, Mn-plant emissions 12%, Power station flyash 6%, Sec. Amm. Nit. 4%, Recovery furnace emissions 3%, Sec. NaCl 2%	Fig 3 Reddy et al., 1997	Total PM ₁₀ concentration 71.9 µg/ m ³
Valencia Park in Nelspruit, South Africa	CMB Receptor Model	Biomass burning emissions 34%, Fugitive soil dust 24%, Sec. Amm. Bisul. 20%, Power station flyash 14%, Recovery furnace emissions 4%, Sec. Amm. Nit. 1%, NaCl 1%, vehicle emissions 1%, Mn-plant emissions 1%	Fig 3 Reddy et al., 1997	Total PM ₁₀ concentration 57.1 µg/ m ³
Randburg, South Africa	CMB Receptor Model	Power station flyash 24%, Domestic coal combustion 22%, Sec. Amm. Sul. 17%, Fugitive soil dust 14%, Sec. Potassium Chloride 10%, Sec. Amm. Nit. 4%, vehicle emissions 4%, Sec. Amm. Chlor. 3%, Iron-arc furnace emissions 2%	Fig 3 Reddy et al., 1997	Total PM ₁₀ concentration 34.0 µg/ m ³

Boston, Massachusetts	SPCA, APCSRM	Soil 58%, Coarse sulfate 14%, Motor vehicles 7%, Refuse burning 6%, Salt 5%, Oil 2%, Unexplained 8%	Table 4 Thurston & Spencer, 1985	
Coimbra, Portugal	PCA followed by multiple LRA	Soil 48%, Marine (and road salt) 23%, Sec. oil combustion 18%, Vehicles 4%, Coal na.	Table 8 Harrison et al., 1997	PM 0.95-10 μ m
Lahore, Pakistan	PCA followed by multiple LRA	Soil 62%, Sec. oil combustion 18%, Vehicles 2%, Metallurgical processes 2%.	Table 8 Harrison et al., 1997	Total Suspended Solids
Edmonton, Alberta	CMB Receptor Model	Geological Soil 15%, Paved Road Dust 15%, Power Plants 15%, Petroleum Refineries 8%, Cement Industry 4%, Marine Salt 1%, NO ₃ by Atmospheric Reaction 1%, Other 42%	Fig. 4 Cheng et al., 1998	Coarse is for the fraction between 2.5 and 10 μ m
Calgary, Alberta	CMB Receptor Model	Coarse Geological Soil 20%, Paved Road Dust 16%, Cement Industry 11%, Marine Salt 2%, NO ₃ by Atmospheric Reaction 1%, Other 49%	Fig. 4 Cheng et al., 1998	Coarse is for the fraction between 2.5 and 10 μ m

Table 5. Source apportionment results for PM_{2.5} outside Canada

Study Location	Statistical Tool	Source Apportionment Results	Reference	Comments
Mexico City Metropolitan Area	CMB Receptor Model	Vehicles 41%, Oil Refineries 12%, Diesel 6%, Organic Carbon 5%	Fig 1 Vega et al., 1997	Source Day Contribution to PM _{2.5}
Mexico City Metropolitan Area	CMB Receptor Model	Vehicles 37%, Oil Refineries 18%, Diesel 4%, Organic Carbon 3%	Fig 2 Vega et al., 1997	Source Night Contribution to PM _{2.5}
Los Angeles, California	CMB Receptor Model	Sec. Carbon 29%, Amm. Sul. 20%, Amm. Nit. 19%, Diesel 16%, Road Dust 9%, Gas 2%, Marine 1%, Unexplained 4%	Fig 1d Gray et al., 1988	
Houston, Texas	CMB Receptor Model	Sulfate and Cations 43%, Other Carbon 14%, Vehicle Exhaust 7%, Crustal 4%, Steel 3%, Other Metals 2%, Other 27%	Fig 2a Stevens & Pace, 1984	
Detroit, Michigan	Factor Analysis Receptor Model	Sulfate Factor 55%, Motor Vehicles 5%, Incinerator 4%, Oil Burning 3%, Unidentified 33%	Fig 3a Wolff & Korsog, 1985	
Birmingham, England	PCA followed by multiple LRA	Road dust 32%, Vehicular 25%, Secondary/oil combustion 23%, Coal 11%, Incineration 7%	Table 8 Harrison et al., 1997	PM < 2.1 µm
Coimbra, Portugal	PCA followed by multiple LRA	Soil 37%, Vehicular 24%, Secondary/oil combustion 15%, Marine (and road salt) 15%	Table 8 Harrison et al., 1997	PM < 0.95 µm
Edmonton, Alberta	CMB Receptor Model	Transportation 48%, Wood burning 27%, Paved Road Dust 12%, SO ₄ by Atmospheric Reaction 6%, Cement Industry 2%, NO ₃ by Atmospheric Reaction 1%, Other 4%	Fig. 4 Cheng et al., 1998	

Calgary, Alberta	CMB Receptor Model	Wood burning 27%, Transportation 21%, Asphalt Industry 11%, Cement Industry 2%, Paved Road Dust 4%, SO ₄ by Atmospheric Reaction 4%, NO ₃ by Atmospheric Reaction 2%, Other 27%	Fig. 4 Cheng et al., 1998	
Boston, Massachusetts	SPCA, APCSRM	Coal related 40%, Motor vehicles 14%, Oil 12%, Soil 11%, Unexplained 22%	Table 4 Thurston & Spencer, 1985	

7.3 Conclusions and Recommendations for Some Apportionment Methods

The CMB model for source apportionment of emission sources is not the only statistical tool but it is the most widely used and has the longest history (ca. 20 yrs). It can easily be combined with other multivariate techniques such as principal components analysis for data exploration and validation of results. The CMB model is a good point of departure even when little or no local source profiles (preferable) are available; major sources can be identified and monitoring stations planned for predicting concentrations of specific chemical species.

National and regional studies have been completed in Canada since the early 1980s, mainly using the CMB approach and/or dispersion models. One study indicated that results between CMB and dispersion models can be quite different.

8. DATA GAPS AND FUTURE RESEARCH

Ambient: The number of sites collecting ambient PM information is limited. More sites within Edmonton and Calgary are needed for better consideration of the fate and transport of the primary particulates and better assessment of the formation of the secondary particulates. Also more species, such as organic carbon and elemental carbon, are needed.

Ambient data should also be collected outside the cities' limits in order to determine the background concentration of particulates.

Sources: Profiles from Alberta sources should be collected for better use of the results of CMB modeling and representing the Alberta situation. Detailed studies should be further conducted on the major contributing sources once they are identified.

Analytical: Methods capable of detection and quantification of a maximum number of species should be developed and adopted. Speciation dealing with organic compounds could be accomplished with combination of the inorganic parameters. Methods should be developed to distinguish between diesel and gasoline engine emissions.

Modeling: The CMB method requires considerable expert input. It also requires the user to accept certain assumptions which can be difficult. Therefore, efforts to enhance the CMB approach have been taken at ARC - Vegreville. Regardless of the method used, having local source profiles will greatly improve the confidence by the user with the CMB results.

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